Synthesis of Ordered Polyamide by Direct Polycondensation. 4

Mitsuru Ueda* and Hitoshi Sugiyama

Department of Materials Science and Engineering, Faculty of Engineering, Yamagata University, Yonezawa, Yamagata 992, Japan

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ABSTRACT: Ordered (-aadcbbcd-) polyamides were prepared by the direct polycondensation of a pair of symmetric monomers (XabX), bis(2,4,6-trichlorophenyl) isophthalate or bis(2,4,6-trichlorophenyl) adipate (XaaX) and 5-nitroisophthalic acid (XbbX), with a nonsymmetric monomer (YcdY), 4-aminobenzohydrazide, using the activating agent diphenyl (2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate. The polycondensation was carried out by mixing the monomers all at once, yielding the ordered polyamide with inherent viscosities up to 0.30 dL/g. The authentic ordered and random polyamides were prepared to verify the structures of ordered polyamide. The microstructures of polyamides obtained were investigated by means of ^{13}C NMR spectroscopy, and it has been found that the polyamides obtained had the expected ordered structures. Furthermore, the model reactions were studied in detail to demonstrate the feasibility of ordered polyamidation.

Introduction

Most condensation polymers are prepared by reactions between two different bifunctional symmetric monomers. However, the synthesis of condensation polymers from a symmetric (YccY) and a nonsymmetric (XabX) monomer has been only slightly explored.[1]

Our group has recently initiated a synthesis of ordered polymer from nonsymmetric monomers by direct polycondensation. In the preceding papers,[2] we reported a successful synthesis of ordered polyamides (head-to-head or tail-to-tail) from a symmetric monomer and a nonsymmetric monomer[2a,b] and ordered polyamides (head-to-tail) from a symmetric monomer and a nonsymmetric monomer or a pair of two symmetric monomers.[2c]

Our next target was the synthesis of ordered polyamide (-bacd-) from two nonsymmetric monomers, XabX and YcdY, by direct polycondensation. Recently, Suter et al.[3] studied theoretical aspects of systems with two nonsymmetric monomers. One can write the relevant elementary reactions and the relative reactivities of functional groups of both monomers for this polymerization as follows:

$$-aX + Yc- \xrightarrow{k_{ac}} -ac- + XY, \quad r_1 = k_{ad}/k_{ac}, \quad 0 \le r_1 \le 1$$

$$-aX + Yd- \xrightarrow{k_{ad}} -ad- + XY, \quad r_2 = k_{bc}/k_{ac}, \quad 0 \le r_2 \le 1$$

$$-bX + Yc- \xrightarrow{k_{bc}} -bc- + XY, \quad r_3 = k_{bd}/k_{ac}, \quad 0 \le r_3 \le 1$$

$$-bX + Yd- \xrightarrow{k_{bd}} -bd- + XY$$

The polyamide with -bacd- order is obtained when the relative reactivity ratios r_1 and r_2 are both smaller than unity (less than 0.01). In this case, the first intermediate is XbacdY, which will later polymerize stoichiometrically to the fully ordered (-bacd-) polymer.

This article describes a successful synthesis of ordered polyamide by the direct polycondensation of a pair of symmetric monomers (XabX), bis(2,4,6-trichlorophenyl) isophthalate or bis(2,4,6-trichlorophenyl) adipate (XaaX) and 5-nitroisophthalic acid (XbbX), with a nonsymmetric monomer (YcdY), 4-aminobenzohydrazide, using the activating agent diphenyl (2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate (1).

Experimental Section

Materials. *N*-Methyl-2-pyrrolidone (NMP) was purified by vacuum distillation and stored over 4-Å molecular sieves. 5-Nitroisophthalic acid (**8a**), isophthalic acid (**8b**), and adipic acid (**8c**) were purified by recrystallization from ethanol-water or water. 4-Aminobenzohydrazine (**9**) was prepared from methyl-4-aminobenzoate and hydrazine monohydrate according to the reported procedure.[4] Other reagents and solvents were obtained commercially and used as received.

The activating agent diphenyl (2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate (1) was prepared according to the reported procedure.[5]

2,4,6-Trichlorophenyl Benzoate (3). To a stirred solution of 2,4,6-trichlorophenol (1.18 g, 6.0 mmol) and benzoyl chloride (0.84 g, 6 mmol) in NMP (5 mL) was added dropwise triethylamine (TEA) at 0 °C. After being stirred for 10 min, the reaction mixture was poured into 5% aqueous sodium hydrogen carbonate (100 mL). The product which precipitated was collected and dried in vacuo. The yield was 1.8 g (100%). Recrystallization from ethanol afforded white needles, mp 66-67 °C. IR (KBr): ν 1755 (C=O), 1265 cm^{-1} (CO). Anal. Calcd for $C_{13}H_7Cl_3O_2$: C, 51.75; H, 2.33. Found: C, 51.72; H, 2.42.

Bis(2,4,6-Trichlorophenyl) Isophthalate (7a). This compound was prepared by the condensation of trichlorophenol with isophthaloyl chloride as described above. The yield was 80%. Recrystallization from benzene-hexane gave white needles, mp 166-168 °C. IR (KBr): ν 1750 cm^{-1} (C=O). Anal. Calcd for $C_{20}H_8Cl_6O_4$: C, 45.75; H, 1.53. Found: C, 46.01; H, 1.68.

Bis(2,4,6-trichlorophenyl) Adipate (7b). This compound was prepared from 2,4,6-trichlorophenol and adipoyl chloride. The yield was 95%. Recrystallization from *n*-hexane yielded white needles, mp 101-103 °C. IR (KBr): ν 1770 cm^{-1} (C=O). Anal. Calcd for $C_{18}H_{12}Cl_6O_4$: C, 42.81; H, 2.39. Found: C, 43.14; H, 2.48.

Competitive Reaction of Anisic Acid (2a) and 3 with Benzohydrazide (4b). Activating agent 1 (0.422 g, 1.1 mmol) was added to a solution of **2a** (0.160 g, 1.0 mmol), **3** (0.302 g, 1.0 mmol), and **4b** (0.136 g, 1.0 mmol) in NMP (1 mL) at room temperature. The solution was stirred for 10 min and poured into 1% aqueous sodium carbonate. The precipitate was filtered, washed with water, and dried. The crude product was chromatographed on silica gel (C-300) using chloroform as eluent to remove unreacted **3**. The product was identified as *N'*-benzoyl-4-methoxybenzohydrazide (5b). The yield was 0.245 g (91%), mp 195-197 °C. IR (KBr): ν 1670, 1624 cm^{-1} (C=O). Anal. Calcd for $C_{15}H_{14}N_2O_3$: C, 66.65; H, 5.22; N, 10.36. Found: C, 66.38; H, 5.22; N, 10.25.

Competitive Reaction between 4b and Aniline with Benzoic Acid (2b). To a solution of **2b** (0.122 g, 1.0 mmol),

* To whom correspondence should be sent.

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TEA (0.14 mL, 1.0 mmol), aniline (0.09 mL, 1.0 mmol), and **4b** (0.136 g, 1.0 mmol) in NMP (1 mL) was added 1 (0.422 g, 1.1 mmol) at room temperature. The solution was stirred for 10 min and poured into 1% aqueous sodium carbonate. The precipitate was filtered, washed with water, and dried. The product was identified as *N'*-benzoylbenzohydrazide (**5b**). The yield was 0.230 g (97%), mp 241–242 °C (lit.[6] mp 238–240 °C). IR (KBr): ν 1633, 1672 cm^{-1} (C=O).

Model Compounds. The following model compounds were prepared from the corresponding acyl chlorides and amines.

***N',N'*-Dibenzoylisophthalodihydrazide (10b)**: mp 293–294 °C (from acetic acid). Anal. Calcd for $C_{22}H_{18}N_4O_4$: C, 65.66; H, 4.5; N, 13.92. Found: C, 65.57; H, 4.67; N, 13.72.

5-Nitroisophthalanilide (10c): mp 283–284 °C (from methanol). Anal. Calcd for $C_{20}H_{15}N_3O_4$: C, 66.47; H, 4.18; N, 11.62. Found: C, 66.21; H, 4.27; N, 11.57.

***N',N'*-Dibenzoyl-5-nitroisophthalodihydrazide (10d)**: mp 284–285 °C (methanol). Anal. Calcd for $C_{22}H_{17}N_5O_6$: C, 59.06; H, 3.82; N, 15.65. Found: C, 59.46; H, 3.67; N, 15.85.

***N',N'*-Dibenzoyladipodihydrazide (10f)**: mp 251–252 °C (DMF–methanol). Anal. Calcd for $C_{20}H_{22}N_4O_4$: C, 62.81; H, 5.79; N, 14.65. Found: C, 62.78; H, 5.78; N, 14.39.

Authentic Ordered Polyamide 13a. *N',N'*-Bis(4-aminobenzoyl)-5-nitroisophthalodihydrazide (11): A solution of **8a** (0.589 g, 3.0 mmol), TEA (0.84 mL, 6.0 mmol), and 1 (2.53 g, 6.6 mmol) in NMP (3 mL) was added dropwise to a solution of **9** (0.907 g, 6.0 mmol) in NMP at room temperature. After 30 min of stirring, the mixture was poured into 1% aqueous sodium hydrogen carbonate. The product precipitated was collected by filtration, washed with water, and refluxed in methanol. The residue was 1.28 g (90%), mp 305–306 °C. IR (KBr): ν 1605 (C=O), 3215 cm^{-1} (NH). Anal. Calcd for $C_{22}H_{19}N_7O_6$: C, 55.34; H, 4.01; N, 20.53. Found: C, 54.74; H, 4.08; N, 20.14.

11 (0.238 g, 0.5 mmol) was dissolved in NMP (2.5 mL) at room temperature. The solution was cooled in a dry ice–acetone bath, to which was added isophthaloyl chloride (**12a**) (0.101 g, 0.5 mmol) in one portion, and the cooling bath was changed to ice–water. The mixture was stirred for 30 min at 0 °C and then for 1 h at room temperature. The resulting polymer solution was diluted with NMP (2 mL), and polymer was precipitated by pouring the solution into methanol. After thorough washing with methanol and drying, the polymer weighed 0.326 g (100%). The inherent viscosity of the polymer in NMP was 0.71 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. IR (film): ν 1650 (C=O), 3260 cm^{-1} (NH). Anal. Calcd for $(C_{30}H_{21}N_7O_8)_n$: C, 59.3; H, 3.48; N, 16.13. Found: C, 59.13; H, 3.26; N, 15.69.

Authentic Ordered Polyamide 13b. This polymer was prepared by the polycondensation of 11 (0.239 g, 0.5 mmol) with adipoyl chloride (**12b**) (0.0915 g, 0.5 mmol) in NMP as described above. The yield was 0.264 g (100%). The inherent viscosity of the polymer in NMP was 0.41 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. IR (film): ν 1655 (C=O), 3260 cm^{-1} (NH). Anal. Calcd for $(C_{28}H_{25}N_7O_8{\cdot}1.8H_2O)_n$: C, 55.05; H, 4.61; N, 15.81. Found: 54.83; H, 4.51; N, 15.48.

Random Polyamide 14a. Activating agent 1 (0.843 g, 2.2 mmol) was added to a solution of **8a** (1.06 g, 0.5 mmol), **8b** (0.083 g, 0.5 mmol), **9** (0.151 g, 1.0 mmol), and TEA (0.28 mL, 2.0 mmol) in NMP (1 mL). The mixture was stirred at room temperature for 8 h and at 80 °C for 8 h. The resulting solution was diluted with NMP (2 mL) and poured into methanol (100 mL). The polymer was collected and dried in vacuo at 80 °C. The yield was 0.326 g (100%). The inherent viscosity of the polymer in NMP was 0.40 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. IR (film): ν 1655 (C=O), 3255 cm^{-1} (NH). Anal. Calcd for $(C_{30}H_{21}N_7O_8)_n$: C, 59.3; H, 3.48; N, 16.13. Found: C, 59.72; H, 3.31; N, 15.68.

Random Polyamide 14b. This polymer was prepared from **8a** (0.106 g, 0.5 mmol), **8c** (0.0731 g, 0.5 mmol), TEA (0.28 mL, 2.0 mmol), and **9** (0.151 g, 1.0 mmol) in the presence of 1 (0.843 g, 2.2 mmol) as described above. The yield was 0.276 g (100%). The inherent viscosity of the polymer in NMP was 0.37 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. IR (film): ν 1655 (C=O), 3260 cm^{-1} (NH). Anal. Calcd for $(C_{28}H_{25}N_7O_8)_n$: C, 55.87; H, 4.55; N, 16.28. Found: C, 55.25; H, 4.44; N, 15.75.

Polyamide 15a from 8a, 7a, and 9. To a solution of **8a** (0.106 g, 0.5 mmol) and **7a** (0.262 g, 0.5 mmol) in NMP (1 mL) were added all at once **9** (0.151 g, 1.0 mmol), TEA (0.14 mL, 1.0 mmol), and 1 (0.422 g, 1.1 mmol). The mixture was stirred at room temperature for 1 h. To the resulting solution was added 1-hydroxybenzotriazole (HOBt) (0.0153 g, 0.1 mmol). Then the solution was stirred at 80 °C for 7 days. The polymer was isolated as described above. The yield was 0.279 g (92%). The inherent viscosity of the polymer in NMP was 0.25 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. IR (film): ν 1655 (C=O), 3260 cm^{-1} (NH). Anal. Calcd for $(C_{30}H_{21}N_7O_8)_n$: C, 59.3; H, 3.48; N, 16.13. Found: C, 59.21; H, 3.27; N, 15.86.

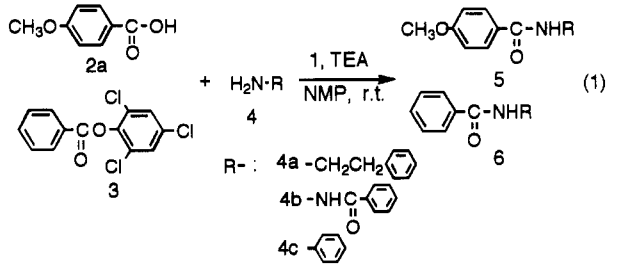
Polyamide 15b from 8a, 7b, and 9. **8a** (0.211 g, 1.0 mmol), **7b** (0.505 g, 1.0 mmol), TEA (0.28 mL, 1.0 mmol), and **9** (0.302 g, 2.0 mmol) were combined in the presence of 1 (0.848 g, 2.2 mmol) and HOBt (0.031 g, 0.2 mmol) as described above. The yield was 0.610 g (100%). The inherent viscosity of the polymer in NMP was 0.30 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. IR (KBr): ν 1655 (C=O), 3260 cm^{-1} (NH). Anal. Calcd for $(C_{28}H_{25}N_7O_8{\cdot}1.8H_2O)_n$: C, 54.25; H, 4.69; N, 15.81. Found: C, 54.95; H, 4.49; N, 15.64.

Measurements. The infrared spectra were recorded on a Hitachi I-5020-FT-IR spectrophotometer, and the NMR spectra on a JEOL EX270 (270 MHz) spectrometer. Viscosity measurements were carried out by using an Ostwald viscometer at 30 °C. Thermal analyses were performed on a Seiko SSS 5000 TG/DTA 200 thermal analyzer at a heating rate of 5 °C min^{-1} for thermogravimetric analysis (TG).

Results and Discussion

The choice of nonsymmetric dicarboxylic acids and diamines is most important in the preparation of the ordered polyamides by direct polycondensation using the activating agent 1.

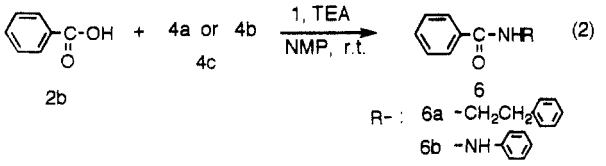
Selection of Nonsymmetric Dicarboxylic Acid. The selective amidation of carboxylic acids would be difficult using activating agent 1 because of the small difference of pK_a values between carboxylic acids. Thus, we planned to employ a nonsymmetric monomer having a carboxylic acid and a carboxylic acid derivative. In a previous paper,[7] we reported polyamide synthesis by 1-hydroxybenzotriazole-catalyzed polycondensation of active aromatic diesters with aromatic diamines, where bis(2,4,5-trichlorophenyl) isophthalate reacted slowly with aromatic diamines at 70 °C, but gave a high molecular weight of polyamide. Therefore, the competitive reaction between anisic acid (**2a**) and 2,4,6-trichlorophenyl benzoate (**3**) with amines (**4**), such as phenethylamine (**4a**), benzohydrazide (**4b**), and aniline (**4c**), was carried out at room temperature for 10 min in the presence of 1 (eq 1). Selective amidations



were observed in all cases, and compounds **5**, that is, *N*-phenethyl-4-methoxybenzamide (**5a**), *N'*-benzoyl-4-methoxybenzohydrazide (**5b**), and 4-methoxybenzanilide (**5c**), were obtained in quantitative yields.

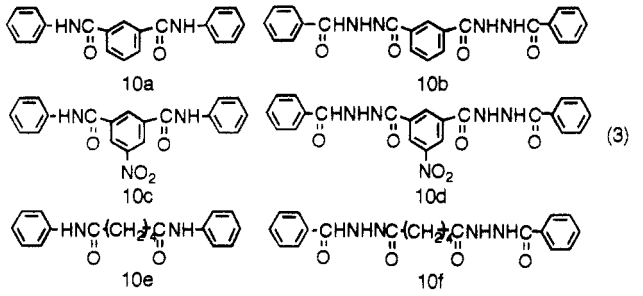
Selection of Nonsymmetric Amines. We reported that there is a linear relationship with a slope of 1 between log k and pK_a of aniline derivatives for the reaction of benzoic acid with various anilines in NMP in the presence of 1.[8] Therefore, the competitive reactions between **4a** (pK_a = 10) or **4b** (about pK_a = 7) and **4c** (pK_a = 4) with benzoic acid (**2b**) were carried out at room temperature for 5 min in the presence of 1 and gave compounds **6**, that is, *N*-phenethylbenzamide (**6a**) and *N'*-benzoylbenzohy-

drazide (**6b**), respectively, in quantitative yields (eq 2). On



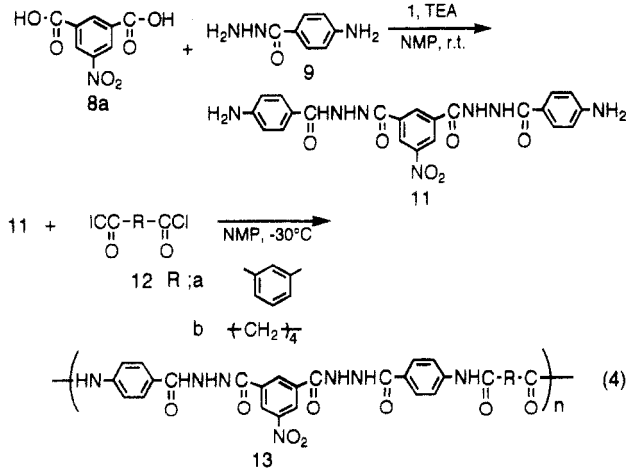
the basis of these model reactions and the availability of reagents, we decided to use a pair of dicarboxylic acid derivatives, bis(2,4,6-trichlorophenyl) isophthalate (**7a**) or bis(2,4,6-trichlorophenyl) adipate (**7b**) (XaaX) and 5-nitroisophthalic acid (XbbX) (**8a**) as a nonsymmetric monomer (XabX), and 4-aminobenzohydrazide (**9**) as a nonsymmetric monomer (YcdY).

The model compounds depicted in eq 3 were prepared from the corresponding acyl chlorides and amines in order to clarify the structure of polymers obtained.



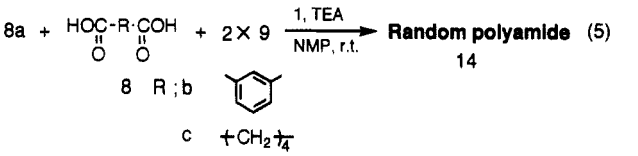
Polymer Synthesis

Synthesis of Ordered Polyamide 13. The authentic ordered polyamide **13** was prepared by the low-temperature solution polycondensation of isophthaloyl chloride (**12a**) or adipoyl chloride (**12b**) with *N'*,*N'*-bis(4-aminobenzoyl)-5-nitroisophthalodihydrazide (**11**), which was obtained from **8a** and **9** (eq 4). The polycondensations proceeded smoothly, giving polyamides **13** with inherent viscosities of 0.71 dL/g and 0.41 dL/g, respectively.

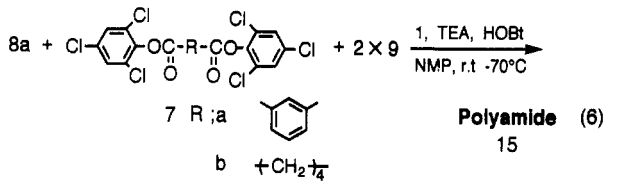


Synthesis of Random Polyamide 14. Random polyamide **14a** with an inherent viscosity of 0.40 dL/g was synthesized from **8a**, isophthalic acid (**8b**), and **9** in the presence of **1** by mixing the three monomers at once (eq 5). The same procedure was carried out except for replacement of **8b** with adipic acid (**8c**) for the preparation of random polyamide **14b** with an inherent viscosity of 0.34 dL/g.

Synthesis of Ordered Polyamide 15. As briefly described in the Introduction, the ordered polymer is obtained when the monomers are mixed very rapidly.

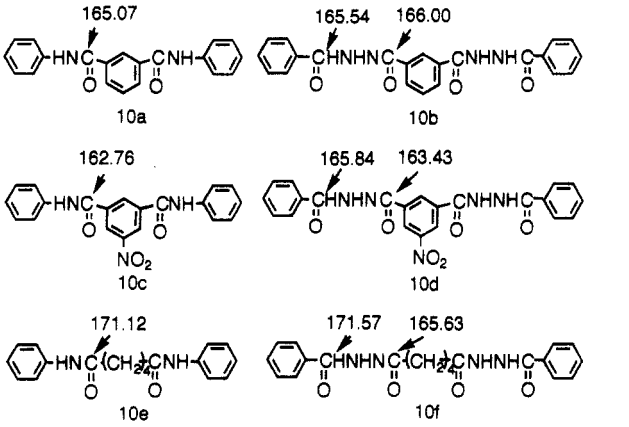


Therefore, the synthesis of the ordered polyamide (**15a**) was carried out by mixing three monomers, **8a**, **7a**, and **9**, all at once in the presence of **1** in NMP at room temperature and then at 70 °C (eq 6). The polycondensation proceeded slowly and gave polyamide **15a** with an inherent viscosity of 0.25 dL/g. In the same way, polyamide **15b** with an inherent viscosity of 0.30 dL/g was obtained from **7b**, **8a**, and **9**.



Polymer Characterization. The IR spectra of the polyamides were consistent with those of model compounds and known analogues. All polyamides prepared showed characteristic NH, amide I, and amide II bands in the ranges 3220–3320, 1630–1640, and 1520–1540 cm^{-1}, respectively. Elemental analyses also supported the formation of the expected polymers.

The microstructure of polymers was determined by means of ^{13}C NMR spectroscopy. ^{13}C NMR chemical shifts of amide carbonyl groups for model compounds are as follows.



The ^{13}C NMR spectra of authentic ordered polyamide **13a**, random polyamide **14a**, and polyamide **15a** prepared by direct polycondensation are presented in Figure 1. The signals of carbon nuclei in amide carbonyl groups for polyamide **13a** appeared at 165.3, 165.2, and 163.4 ppm, and those for random polyamide **14a** were observed at 165.3, 163.4, and 163.1 ppm. However, six peaks would be expected to appear for polyamide **14a**. It can be assumed that the difference in the chemical shifts at around 165.3 ppm is so small that three peaks overlap. These peaks were assigned, as shown in the inset in Figure 1, on the basis of assignments for model compounds. Furthermore, the spectrum of authentic ordered polyamide is identical to that of polyamide **15a**. These findings clearly indicate that the direct polycondensation of **8a**, **7a**, and **9** produced the desired ordered polyamide **15a**.

In a similar manner, the ^{13}C NMR spectra of authentic ordered polyamide **13b**, random polyamide **14b**, and polyamide **15b** are shown in Figure 2. The spectrum of polyamide **15b** is identical to that of polyamide **13b**. Six

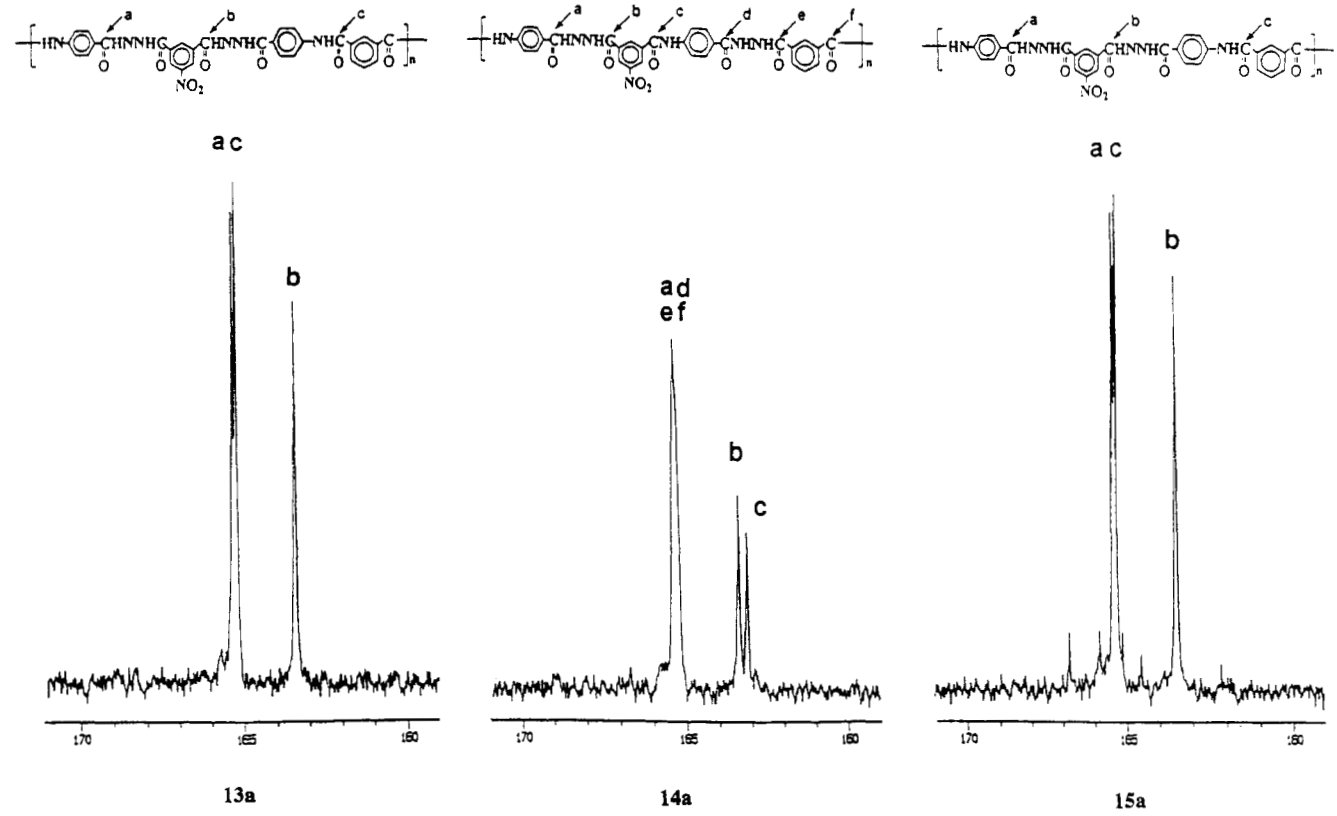


Figure 1. ^{13}C NMR spectra of polyamides **13a**, **14a**, and **15a** in $[(CD_3)_2SO]$ at 25 °C.

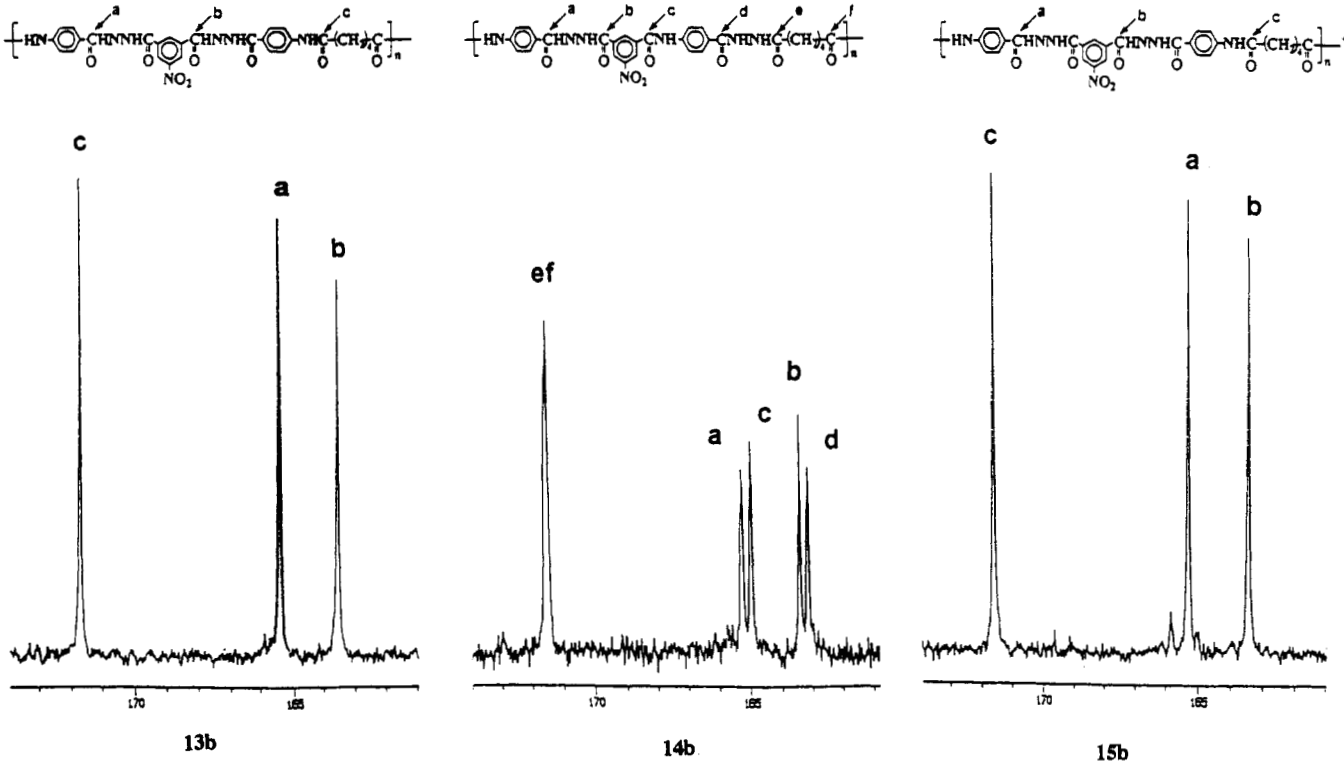


Figure 2. ^{13}C NMR spectra of polyamides **13b**, **14b**, and **15b** in $[(CD_3)_2SO]$ at 25 °C.

peaks of carbon nuclei in amide carbonyl groups should be observed for random polyamide **14b**; but polyamide **14b** showed five peaks at 165.2, 163.4, 163.1, 165.0, and 171.5 ppm probably because two peaks at around 171.5 ppm overlap. These results indicate that the desired ordered polyamide was obtained by direct polycondensation of **8a**, **7b**, and **9** in the presence of **1**.

The polyamides were light yellow solids, soluble in sulfuric acid and dipolar aprotic solvents, such as NMP, DMF, and DMSO, and insoluble in other common organic solvents.

The thermal stability of the polyamide was examined by thermogravimetry (TG) and differential thermal analysis (DTA). Typical traces for polymer **13a** are shown in Figure 3. The DTA trace has an endothermic peak at 335 °C and an exotherm at 465 °C, which correlated well with the weight loss temperatures in the TG trace. The rapid weight loss, observed at 295–345 °C in the TG trace,

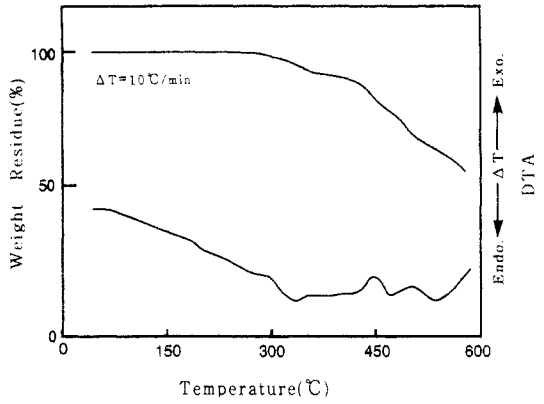


Figure 3. TG and DTA traces of polyamide **15a** in nitrogen.

amounted to 7% of the weight of polymer **13a**. This value is in good agreement with the value of weight loss (5.9%) calculated from the elimination of water due to the 1,3,4-oxadiazole ring formation. The second weight loss occurred at around 440 °C, which corresponds to the degradation of polymer **13a**. We expected differences in their properties owing to different regularity. However, no difference in the solubility and thermal stability among these polyamides can be detected. Pino et al. observed similar behavior in studies of the influence of constitutional isomerism on the physical properties of polycondensates and reported that unsubstituted polyamide might no be very suitable because strong effects brought about by extensive interchain NH–OC bonds might mask subtle effects due to isomerism.[1d]

In summary, we have demonstrated that the synthesis of ordered polyamides can be achieved by the direct polycondensation of a pair of symmetric monomers, **8a** and **7** as a nonsymmetric monomer, with a nonsymmetric monomer **9** using activating agent **1**. This polymerization represents the first example of the synthesis of ordered polymer from two nonsymmetric monomers.

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